SOLVATOCHROMIC STUDIES ON 4-(1,4 DIPHENYL-1H-IMIDAZOLE-2-YLTHIO)-2H-CHROMEN-2-ONE

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ABSTRACT

The substituted 1,4-diaryl-2-mercaptoimidazole were synthesized and further converted to on 4-(1,4 diphenyl-1H-imidazole-2-ylthio)-2H-chromen-2-one by nucleophilic substitution reaction, the effect of substituted aryl group on photophysical properties of parent 4-(1,4 diphenyl-1H-imidazole-2-ylthio)-2H-chromen-2-one is studied. Dipole moment in the ground and excited state is estimated by a solvatochromic method using different solvents, variation in the substitutions has little impact such as methyl group when replaced with chloro, the ground state dipole moment has been reduced whereas no such variations have been observed for excited state.

Keywords: Coumarin, Imidazole, Charge Transfer, Absorption Spectra, Emission Spectra

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INTRODUCTION

The absorption and fluorescence of organic molecules in solution are affected by the solvent due to vibrational relaxation, redistribution of electrons in the solvent^{1,4}, inducing the altered dipole moment of the excited state of solute molecule in comparison to ground state after excitation of a molecule by photon. The dipole moment of an excited molecule^{4,5} provides important information on the electronic structure of the molecule in a short-lived state.

The solvatochromic effect on spectral shift is either due to nonspecific (Dielectric rich environment) or due to specific (hydrogen bonding) solute-solvent interactions. These solvatochromic effects on emission spectral positions imply the charge transfer (CT) character of singlet state both in the polar and nonpolar environment⁶ and it can be evaluated using a solvatochromic parameter⁷.

The dielectric constant and hydrogen-bonding capacity of the solvent molecule have an impact on the electronic ground state and excited state of fluorophore therefore the amount of energy gap between them will change as the solvent changes, which alters the position, intensity and shape of absorption and emission spectroscopic bands. If these changes occur in the visible part of the spectrum solvatochromism exhibit changes in colors⁸.

Coumarins are characterized by fluorescence due to UV light absorption, it is also photosensitive, can be altered by natural light. Coumarins are investigated for dual fluorescence⁹. The solvatochromic behavior of imidazoles depends on the polarity of the solvent and the ability of the solvent to form a hydrogen bond^{9,10}. Coumarins substituted at fourth position by imidazoles derivatives have been investigated for dual fluorescence and energy transfer studies study of solvatochromic effect on coumarins is of considerable interest^{11,12}, these behavior oxygen-containing heterocycle with nitrogen functionality arises due to ability to interact with both isotopic and anisotropic solvents^{13,14}.

In the present work, we fused the most biologically important heterocyclic rings, Imidazole in the form of 1,4-Diaryl-2-mercapto Imidazole with 4-chloro-coumarin to get a new moiety. And then we subjected thus fused compound to Ultraviolet and Fluorescence studies using different solvents with different polarities.

EXPERIMENTAL

Material and Methods

The 4-chlorocoumarin was synthesized by treating the 4-hydroxycoumarin with POCl₃. Phenacyl bromides reacting with substituted arylamines yielded substituted N-Aryl benzamide, further reaction with potassium thiocyanate under anhydrous condition yielded desired 1,4-Diaryl-2-mercapto Imidazole. Thus, obtained product 1,4-Diaryl-2-mercapto Imidazole on reaction with 4-chloro-coumarin gave a new

moiety. Melting points were determined by the open capillary method and are uncorrected. IR spectra were recorded on Perkin Elmer spectrum version 10.5.4. ^1H -NMR were recorded on Bruker 400 MHz and Bruker 100 MHz spectrometer using DMSO-d_6 as solvent and TMS as an internal standard. The chemical shifts are expressed in δ ppm. The purity of the compound was checked by T.L.C. Mass was recorded using Shimadzu GCMS-QP2010S. The UV and fluorescence measurements were performed on a UV-Visible spectrometer (λ 365 nm Perkin Elmer) and fluorescence spectrophotometer (Hitachi F-7000, Japan). All chemicals purchased were of analytical grade and were used without further purification unless otherwise stated.

Synthesis of (CMI-5)

1,4-diaryl-2-mercaptoimidazole(1mmol) was dissolved in acetone in presence of anhydrous K_2CO_3 , stirred for half an hour then substituted Coumarin (1 mmol) was added and kept for overnight stirring. The reaction mixture was quenched into ice water thus precipitated product was recrystallized in alcohol.

General Procedure for the Synthesis of Phenacyl Bromide

Acetophenone (11.6g) in 15-20ml of anhydrous ether is taken in an R.B flask. To this catalytic amount of AlCl_3 is added. Bromine(5.12ml) is added dropwise with stirring, the reaction mixture is kept at room temperature. After all, bromine is added, it is treated with pet ether. The gel obtained is kept in ice condition. The phenacyl bromide remains as a solid mass of brownish-yellow crystals.

General Procedure for the Synthesis of Substituted 4-chloro Coumarin

Substituted 4-hydroxy coumarin (3g.) and POCl_3 (4.5ml) were refluxed for an hour and quenched carefully in ice-cold water, upon which dark brown colored precipitate separates, which was then filtered and thoroughly dried. It was crystallized from hexane to obtain orange-colored crystalline compound (2) (Step-1).

General Procedure for the Synthesis of α – anilinoacetophenones

A mixture of phenacyl bromide (1 mmol), appropriate aniline (1.1 mmol), and a pinch of anhydrous Na_2CO_3 or K_2CO_3 were placed in a dry pestle and mortar, and ground thoroughly. After 1 hour, an exothermic reaction took place. A yellow-colored solid so obtained is washed with ice-cold water to remove Na_2CO_3 . Then it is filtered and dried to get the product.

General Procedure for the Synthesis of 1,4-diaryl-2-mercaptoimidazole

α -Anilinoacetophenones (1 mmol), potassium thiocyanate (5 mmol), and *p*-toluenesulphonic acid (5 mmol) were ground vigorously in pestle and mortar. The content is transferred to a conical flask and heated to 80-90°C (on water bath) for 1 hour. A yellow-colored solid was obtained which was washed with water, filtered and dried.

General Procedure for Synthesis of 4-(1,4 diphenyl-1*H* imidazole-2-ylthio)-2*H*-chromen-2-one (CMI-5)

Substituted mercaptoimidazole is synthesized by treating 1,4-diaryl-2 mercaptoimidazole(1mmol) with K_2CO_3 using acetone as a solvent kept under stirring for half an hour. To this reaction mixture of substituted Coumarin (1 mmol) is added, then the reaction is kept stirring overnight. After the completion of the reaction, the reaction mixture is quenched with ice water to get the product. The obtained product has been subjected to various spectral studies.

Detection Method

Dipole moments of 4-(1,4 diphenyl-1*H* imidazole-2-ylthio)-2*H*-chromen-2-one (CMI-1 to CMI-4) in-ground as well as in excited state were determined employing the following method.

Method

The dipole moments of molecule in the ground and excited state were found out by combining the formulations of Bakhshiev and Chamma and Viallet. The eqn.-1 and 3 provide a reasonable description of the solvent effect on absorption and emission.

According to Bakhshiev:¹⁵

$$\bar{\nu}_a - \bar{\nu}_f = S_1 f_1(\epsilon, n) + \text{constant} \quad (1)$$

$$\text{Where, } S_1 = 2(\mu_e - \mu_g)^2 / a^3 hc \quad (2)$$

$$f_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \quad (3)$$

According to Chamma and Viallet¹⁶:

$$(\bar{\nu}_a - \bar{\nu}_f)/2 = S_2 f_2(\epsilon, n) + \text{constant} \quad (4)$$

$$\text{Where, } S_2 = -2(\mu_e^2 - \mu_g^2) / a^3 hc \quad (5)$$

$$f_2(\epsilon, n) = \frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) + \frac{(n^4 - 1)}{2(n^2 + 2)^2} \quad (6)$$

From equations (2) and (5), the values of μ_e and μ_g can be given as,

$$\mu_g = \frac{|S_1 + S_2|}{2} \left(\frac{hca^3}{2S_1} \right)^{1/2} \quad (7)$$

$$\mu_e = \frac{|S_1 - S_2|}{2} \left(\frac{hca^3}{2S_1} \right)^{1/2} \quad (8)$$

Where, μ_g and μ_e are dipole moments of the molecule at the ground and excited state, h is the Plank's constant, c is the velocity of light, By calculating the van der Waals volumes ($V = 4/3\pi a_o^3$) according to Edward method¹⁷.

Thus the ratio of ground-state dipole moment to that of the excited state is given as,

$$\frac{\mu_e}{\mu_g} = \frac{|S_1 - S_2|}{|S_1 + S_2|} \quad (9)$$

S_1 can be obtained from the linear plot of Stokes shift ($\nu_{\text{abs}} - \nu_{\text{em}}$) v/s bulk solvent polarity function $f_1(\epsilon, n)$ and S_2 from $(\nu_{\text{abs}} + \nu_{\text{em}})/2$ v/s bulk solvent polarity function $f_2(\epsilon, n)$ linear plot.

Analytical Discussion

UV-Visible and Fluorescence

4-(4-phenyl-1-*m*-tolyl-1*H*-imidazol-2-ylthio)-2-*H*-chromene-2-one (CMI-1), 4-(4-phenyl-1-*p*-tolyl-1*H*-imidazole-2-ylthio)-2-*H*-chromen-2-one (CMI-2) and 4-(1-(3-chlorophenyl)-4-phenyl-1*H*-imidazol-2-ylthio)-2-*H*-chromen-2-one (CMI-3), 4-(1-(4-chlorophenyl)-4-phenyl-1*H*-imidazol-2-ylthio)-2-*H*-chromen-2-one (CMI-4) are synthesized as in Scheme-I and are as shown in (CMI-1 to CMI-5). Among five compounds four viz CMI-1 to CMI-4 are subjected to UV and fluorescence spectral studies. Toluene, 1,4-dioxane, chloroform, ethyl acetate, acetonitrile THF and DMF are used as solvents and all these are of spectroscopic grade. Solutions prepared are of 10^{-5} M concentration and UV –Visible and fluorescence are recorded at room temperature in all the cases. The UV and fluorescence measurements were performed on a UV-Visible spectrometer (λ 365 nm Perkin Elmer) and fluorescence spectrophotometer (Hitach F-7000, Japan).

Step 1 : Synthesis of 1,4-diaryl-2-mercaptoimidazoles

Step 2: Synthesis of 4 chloro coumarin

Step3 : Synthesis of substituted mercaptoimidazole 7

Scheme I:

Analytical Data of 4-(1,4 diphenyl-1*H* imidazole-2-ylthio)-2*H*-chromen-2-one (CMI-5)

Yellow solid, yield: 77%, m.p = 190°C, Mass(M/Z): 430 (M⁺), 432(M+2); IR (in cm⁻¹): 1720(C=O), 1603 (C=C), 1339 (C-H); ¹H NMR(in ppm): 5.6(1H, s), 8.54(1H, s), 7.4(2H, d), 7.71-7.63(3H, m), 7.79(1H, s).

4-(4-phenyl-1-*m*-tolyl-1*H*-imidazol-2-ylthio)-2*H*-chromen-2-one (CMI-1)

FTIR (in cm^{-1}): 1714.13(C=O lactone); 1554.04(C=C); 2989(C-H); 1451.14(C-C). ^1H NMR δ ppm: 5.63 δ ppm (s, 1H, coumarin C-H); 8.3 δ ppm (s, 1H, imidazole C₁₂-H); 2.27 δ ppm (s, 3H, methyl C-H). Obsd. Mass, $M(m/z)$ =410 (M^+ , %); $M-321=89(100\%)$; $M-27.99=382$; $M-319.05=91.05$; $M-265.08=145.29$; $M-117=233$; $M-333.07=77.03$.

4-(4-phenyl-1-*p*-tolyl-1*H*-imidazol-2-ylthio)-2*H*-chromen-2-one (CMI-2)

FTIR (in cm^{-1}): 1710(C=O lactone); 1553.3(C=C); 3038(C-H); 1595.5(C-C). ^1H NMR δ ppm: 5.59 δ ppm (s, 1H, coumarin C₃-H); 8.36 δ ppm (s, 1H, imidazole C-H); 2.28 δ ppm (s, 3H, methyl C-H). Obsd mass: $M(m/z)$ =410 (M^+ , %); $M-321=89(100\%)$; $M-27.99=382$; $M-319.05=91.05$; $M-265.08=145.29$; $M-117=233$; $M-333.07=77.03$.

4-(1-(3-chlorophenyl)-4-phenyl-1*H*-imidazol-2-ylthio)-2*H*-chromen-2-one (CMI-3)

FTIR (in cm^{-1}): 1720 (C=O lactone); 1552 (C=C); 3023(C-H stretch). ^1H -NMR δ ppm: 5.65 δ ppm (s, 1H, coumarin C₃-H); 8.45 δ ppm (s, 1H, imidazole C₁₂-H); Obsd. Mass. $M(m/z)$ = 430 (M^+ , %); 432($(M+2)^+$, 5%); $M-341=89(100\%)$; $M-212=218$; $M-156=274$; $M-182=248$; $M-309=121$.

4-(1-(4-chlorophenyl)-4-phenyl-1*H*-imidazol-2-ylthio)-2*H*-chromen-2-ones (CMI-4)

FTIR(in cm^{-1}): 1708 (C=O lactones); 1553(C=C); 3048(C-H stretch); 1450(C-C). ^1H NMR: 5.6 δ ppm (s, 1H, coumarin C₃-H); 8.42 δ ppm (s, 1H, imidazole C-H). Obsd. Mass, $M(m/z)$ =430; 432($(M+2)^+$, 5%); $M-341=89(100\%)$; $M-148=282$; $M-156=274$; $M-182=248$; $M-309=121$; $M-349=81$.

4-(1,4 diphenyl-1*H* imidazole-2-ylthio)-2*H*-chromen-2-one (CMI-5)

FT-IR(in cm^{-1}): 1715 (C=O lactone); 1594(C=C); 3110(C-H stretch); 1449.61(C-C). ^1H NMR δ ppm: 5.8 δ ppm (s, 1H, coumarin C₃-H); 8.3 δ ppm (s, 1H, imidazole C-H); 2.4 δ ppm (s, 3H, methyl C-H). ^1H Obsd. Mass: $M(m/z)$ =410(M^+ , %); $M-321=89(100\%)$; $M-27.99=382$; $M-319.05=91.05$; $M-265.08=145.29$; $M-117=233$; $M-333.07=77.03$.

RESULTS AND DISCUSSION

All the five synthesized compounds have been confirmed by comparing the melting points from the literature.^{18,19}

Photophysical Properties of CMI-1 to CMI-4

Refractive index and molar extinction coefficients for the chosen solvents and their polarity function values $f_1(\epsilon, n)$ and $f_2(\epsilon, n)$ are represented in Table-1. The selection of solvent and concentration was due to the solubility of the compounds.

Table-1: Solvent Polarity Parameters of Solvents

Solvent	E	N	$f_1(\epsilon, n)$	$f_2(\epsilon, n)$
1,4-Dioxane	2.22	1.422	0.042	0.308
CHCl ₃	4.81	1.442	0.37	0.49
Ethyl Acetate	6.08	1.372	0.493	0.499
THF	7.52	1.407	0.545	0.547
DMF	38.25	1.43	0.839	0.711
CH ₃ CN	36.64	1.344	0.861	0.665

Absorption Spectra of Compounds CMI-1 to CMI-4

The Stokes Shifts in wavenumbers have been calculated from the obtained UV- Fluorescence data (Figs.- 2 and 3) of the compounds which are presented in Table-2 for CMI-1 to CMI-4. The observed bands for CMI-1 in the range of 310-322 nm (band A) and 264-269 nm (band B) have been assigned to $\pi \rightarrow \pi^*$ transitions which are due to Coumarin¹³ and Imidazole moieties respectively. In a nonpolar solvent 1,4-dioxane, CMI-1 showed a single absorption band at 320 nm, with an increase in the polarity of the solvents, there was no significant change in the position of band B. But a longer wavelength absorption band (band A) has been observed in polar solvents.

Similarly, all the compounds from CMI-2 to CMI-4 have shown two bands. For CMI-2, the bands are observed in the range of 308-322 nm (band A) and 267-287 nm (band B), for CMI-3, 311-320 nm (band A) and 263-284 nm (band B) and CMI-4, 310-325 nm (band A) and 265-289 nm (band B) are due to $\pi \rightarrow \pi^*$ transitions, there is no significant difference observed in the absorption bands of CMI-1 to CMI-4 by increasing the polarity of solvents.

Emission Spectra of Compounds CMI-1 to CMI-4

Emission for all the four Compounds CMI-1 to CMI-4 was performed using the longer excitation wavelength i.e., around 320nm in case of polar solvents (Table-2 and Figs.-4 to 7). In the case of CMI-1 two emission bands have been observed in the range of 357-365 nm and 404-419 nm for all solvents. An increase in solvent polarity has not exhibited any regular variations in the emission of compound CMI-1. For CMI-2, observed emission bands were in the range of 353-366 nm and 405-418 nm for all solvents, there also an increase in solvent polarity that did not show any regular variations in emission maxima position. In the case of CMI-3 and CMI-4 observed emission bands were in the range of 348-378 nm and 399-411 nm and, 355-364 nm and 395-421 nm respectively for all solvents with no variations on polarity change.

The hypsochromic shift observed for the second emission band (404-419 nm) in the case of chloro compounds is because of the different charge distribution in the ground and excited states. Polar aprotic solvents, destabilize the excited states of charge-separated polar chloro compound's excited states as there are no hydrogen-bonding interactions with them instead a dipole-dipole repulsion can be anticipated.

Estimation of Dipole Moments of Compounds CMI-1 to CMI-4 in the Ground and the Excited States

The dipole moments in the ground and excited state of compounds CMI-1 to CMI-4 were calculated using equations (7) and (8) and two graphs have been plotted. Figures-2 and 3 show the variation of stokes shifts ($\bar{\nu}_a - \bar{\nu}_e$) against bulk solvent polarity function $f_1(\epsilon, n)$ and the variation of respective spectral shifts of arithmetic mean of $(\bar{\nu}_a + \bar{\nu}_e)/2$ against bulk solvent polarity function $f_2(\epsilon, n)$ for CMI-1 to CMI-4 from these S_1 and S_2 values are obtained (Table-3).

The dipole moments of excited states of CMI-1 and CMI-2 are 2.46 D and 2.11 D respectively, which are comparable with the excited state dipole moment of CMI-3 and CMI-4 are 2.29 D and 1.62 D. But in the case of CMI-1 and CMI-2, the dipole moments of ground state are 1.37 D and 1.28 D respectively, which shows much difference with the dipole moments of ground states of CMI-3 and CMI-4 are 0.18 D and 0.29 D respectively.

Fig.-2: Absorption Spectra of Compounds CMI-1 to CMI-4 in Different Solvents

Table-2: Absorption and Emission Maxima in Wavelengths (λ_a & λ_e), Wavenumbers ($\bar{\nu}_a$ & $\bar{\nu}_e$), Stoke's Shift ($\bar{\nu}_a - \bar{\nu}_e$) and Arithmetic Mean of ($\bar{\nu}_a$ & $\bar{\nu}_e$) of CMI-1 to CMI-4.

Comp.	Solvent	λ_a (in nm)	λ_e (in nm)	$\bar{\nu}_a$ (in cm^{-1})	$\bar{\nu}_e$ (in cm^{-1})	$\bar{\nu}_a - \bar{\nu}_e$ (in cm^{-1})	$(\bar{\nu}_a + \bar{\nu}_e)/2$ (in cm^{-1})
CMI-1	1,4-Dioxane	320	357	31250	28011	3239	29630
	CHCl_3	320,267	412,365	31250	24271	6979	27760
	Ethyl acetate	318,264	404,357	31446	24752	6694	28099
	THF	310,267	366	32258	27322	4936	29790
	DMF	320,267	419,358	31250	23866	7384	27558
	CH_3CN	322,269	407	31055	24570	6485	27812
CMI-2	1,4-Dioxane	322	355	31055	28169	2886	29612
	CHCl_3	318,267	412,366	31446	24271	7175	27858
	Ethyl acetate	310,267	405,358	32258	24691	7567	28474
	THF	308,287	368	32467	27173	5294	29820
	DMF	322,267	418,354	31055	23923	7132	27489
	CH_3CN	314,267	399,353	31847	25062	6785	28454
CMI-3	1,4-Dioxane	320	358	31250	27932	3318	29591
	CHCl_3	315,264	411,378	31746	24330	7416	28038
	Ethyl acetate	319,263	412,361	31347	24271	7076	27809
	THF	311,284	411,348	32154	24330	7824	28242
	DMF	318,265	419,354	31446	23866	7580	27656
	CH_3CN	318,269	399,359	31446	25062	6384	28254
CMI-4	1,4-Dioxane	325	364	30769	27472	3297	29120
	CHCl_3	320,267	412,358	31250	24271	6979	27760
	Ethyl acetate	312,268	410,361	32051	24390	7661	28220

	THF	310,289	361	32258	27700	4558	29979
	DMF	316,265	421,355	31645	23752	7893	27698
	CH ₃ CN	320,267	395	31250	25316	5934	28283

Fig.-3: Emission Spectra of Compounds CMI-1 to CMI-4 in Different Solvents

In case CMI-1 to CMI-4, sulfur atom at C₄ of Coumarin facilitates the movement of electrons from Imidazole to lactone ring of Coumarin, thus by competing with the resonance of π electrons afforded by the aromatic ring. The competition in resonance set by sulfur atom both in Imidazole and Coumarin reduces the dipole moments of hybrids as shown in Fig.-4.

However, changes in the substitutions have a little impact such as methyl group when replaced with chloro, the ground state dipole moment has been reduced to 4-5 times, which is due to negative inductive effect whereas no such variations have been observed for excited-state dipole moments as there are no changes due to delocalization.

Fig.-4

Fig.-5: (A) Variation of Stocks Shift with $f_1(\epsilon, n)$ and (B) Variation of Arithmetic Mean of $\bar{\nu}_a$ and $\bar{\nu}_e$ with $f_2(\epsilon, n)$ for CMI-1

Fig.-6: (A) Variation of Stocks Shift with $f_1(\epsilon, n)$ and (B) Variation of Arithmetic Mean of $\bar{\nu}_a$ and $\bar{\nu}_e$ with $f_2(\epsilon, n)$ for CMI-2

Fig.-7: (A) Variation of Stocks Shift with $f_1(\epsilon, n)$ and (B) Variation of Arithmetic Mean of $\bar{\nu}_a$ and $\bar{\nu}_e$ with $f_2(\epsilon, n)$ for CMI-3

Fig.-8: (A) Variation of Stocks Shift with $f_1(\epsilon, n)$ and (B) Variation of Arithmetic Mean of $\bar{\nu}_a$ and $\bar{\nu}_e$ with $f_2(\epsilon, n)$ for CMI-4

Table-3: Onsagar cavity radius (a_0), Slopes from different parameters (S_1 and S_2), ground state (μ_g) and excited state (μ_e) for CMI-1 to CMI-4.

Compound	$a_0(\text{\AA})$	S_1	S_2	$\mu_g(\text{D})$	$\mu_e(\text{D})$	μ_e/μ_g
CMI -1	4.36	1442.6	-5094.2	1.3796	2.4698	1.7902
CMI-2	4.36	1109.5	-4498.2	1.2803	2.1187	1.6548
CMI-3	4.39	5737	-4867.8	0.1878	2.2905	12.2018
CMI-4	4.39	4423.9	-3078.3	0.2907	1.6211	5.5765

CONCLUSION

Two absorption bands have been observed for Imidazole – Coumarin hybrids. CMI-1 to CMI-4 viz 3.A single emission band has been observed for CMI-1 to CMI-4 for nonpolar solvents and two emission

bands have been observed in polar solvents. There is no significant difference in excited state dipole moments of CMI-1 to CMI-4. There is a drastic difference between ground state dipole moments of CMI-1 and CMI-2 to CMI-3 and CMI-4. Variation in the substitutions has shown observable effects such as methyl group when replaced with chloro, the ground state dipole moment has been reduced to 4-5 times, which is due to negative inductive effect.

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